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Fabrication of ceramic component using constrained surface Microstereolithography

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Abstract

Microstereolithography (MSL) is one of the solid free form fabrication (SFF) techniques which involve fabrication of 3 dimensional (3D) objects by means of laser assisted photopolymerization of resin. The resolution and capability to fabricate high aspect ratio structures makes it suitable technique for the fabrication of Micro Electro Mechanical Systems (MEMS) and biomedical devices. Silicon micromachining technique on the other hand has the limitation in fabricating high aspect ratio structures. Also, the ability to fabricate 3D components using wide range of resins makes MSL a versatile technique. Recently resins loaded with ceramic particles have been used to fabricate sub millimetre ceramic devices for MEMS application. However challenge of processing ceramics lies in reducing the viscosity of the suspension for successful recoating and achieving the minimum layer thickness to improve resolution of the part. In the present study ceramic suspensions is prepared using carboxylic acid as dispersant and 1, 6 Hexanediol diacrylate resin. A ceramic structure containing three layers of 50 microns each was fabricated using constrained surface technique and merits and limitations of this technique were investigated.

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Keywords: Microstereolithography;constrained surface;Surface modified alumina; Shearthinning; viscosty

1. Introduction

Micro Electro Mechanical System (MEMS) devices have been found in many sensing applications such as chemical and biological sensors. These MEMS devices are fabricated using micromachining processes which are

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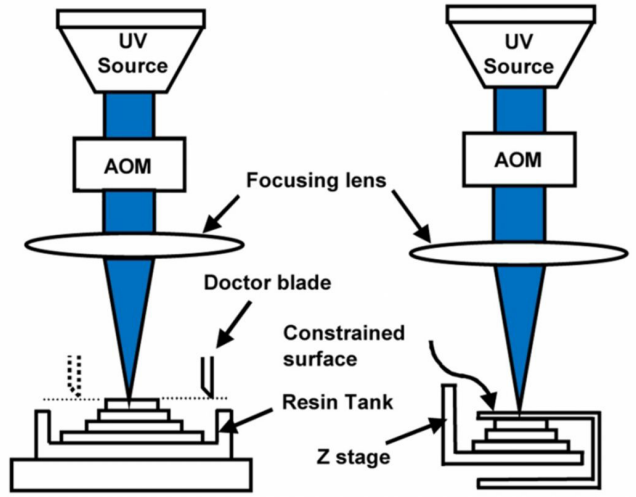
mainly based on soft lithography technique. These techniques provide higher resolution but involve the use of costly mask and limited capability to fabricate true 3D components [J Stampfl et al. 2008]. Currently 2-Photopolymerization process (2PP) is known to be a free form fabrication process with very high resolution [Satoshi Kawata et al. 2001]. In 2PP process the resolution much beyond the diffraction is achieved by controlling the laser pulse energy and number of applied pulses. However the main limitations of 2PP are low writing speed and maximum height of the fabricated parts [J Stampfl et al 2008]. Another SFF process X-ray lithography was developed to fabricate high aspect ratio microstructures [Christophe Marques 1997] but it couldn't find industrial applications due to limited accessibility to industries and high operational cost. In the year 1992 Ikuta et al. (1993) introduced a novel microfabrication process 'Microstereolithography' to fabricate high aspect ratio structures. This process has been applied for fabricating micro-fluidics devices for biomedical applications where the feature resolution is in the range of 1-10 microns. These 3D components are fabricated in microstereolithography by polymerizing a photosensitive resin with computer controlled laser scanning technique. The spot size of laser used to photo polymerize liquid resin is of the order of 1-2 microns [Chrristope Provin et al. 2003; X. Zhang et al. 1993]. The ability to fabricate wide range of materials makes MSL as a versatile technique to fabricate high aspect ratio structures.

Recently some research groups reported fabrication of complex 3D ceramic parts in millimeter and sub millimeter range using microstereolithography apparatus [X. Zhang et al. 1999; X.N. Jiang et al. 2000; S. Monneret et al. 2002; Arnaud Bertsch et al. 2004]. When ceramic particles are dispersed in a (photosensitive) resin the resulting fluid will be a thick paste. During fabrication of 3D structures successive layer recoating becomes an issue owing to high viscosity of suspension. There are two methods available for successive recoating of ceramic suspension. One method uses a doctor blade technique to coat a uniform layer on the top of the previously fabricated layer.(Refer Fig. 1.) Doctor blade utilizes shear thinning behaviour of ceramic suspension and the blade speed is adjusted such that suspension can be spread easily attaining the lowest apparent viscosity at close shear rate. Equation which relates velocity of blade (v), layer thickness (t) and shear rate (γ) is given as follows [Olivier Dufaud et al. 2002].

$$Shear\ rate(\gamma) = \frac{v}{t} \tag{1}$$



(a) (b)

Figure 1.(a) Scanning Microstereolithography with free surface (doctor blade) technique and (b)with constrained surface technique

Since thickness of recoated layer is of the order of 10-20 microns and amount of pure resin deposited on top of the previous layer is very less, doctor blade or scraper cannot be used as it may destroy the previously fabricated

layers [Arnaud Bertsch et al. 2000]. However in case of thick ceramic suspension scraper becomes inevitable as suspension too thick to level itself due to gravity. Hence there should be some device to maintain a required layer thickness before fabrication. At present the methods which are available in MSL system are doctor blade (flexible scraper) and a constrained surface technique .Fig 1.a. shows schematic of scanning MSL equipped with doctor blade and fig 1(b) shows MSL with constrained surface. MSL z stage will confine a fixed amount suspension against fixed surface (constrained surface), the schematic of which is shown in fig. 1 (b).

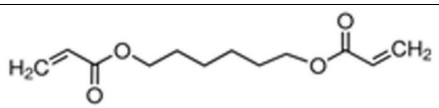
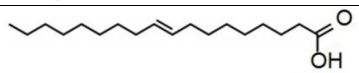
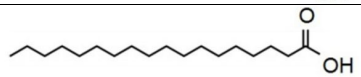
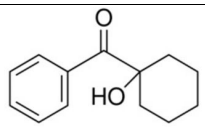
In the present study we have used constrained surface to fabricate 3D ceramic parts in indigenously developed scanning MSL apparatus and evaluated its merits and limitations. Alumina is selected as ceramic material because of excellent thermal and mechanical properties. Suspension was prepared with solid loading of 0.35 volume fraction to avoid any sintering related cracks.

2. Experimental Procedure

2.1 Materials

The ceramic powder used in this study was alumina (Almatis, RG 4000,density 3.9 g/cm^3) with mean particle size d_{50}= 0.45 microns and specific surface area 8.2 m^2/g (measured from BET). Two types of dispersants were used to modify the particle surface from hydrophilic nature to hydrophobic. Oleic acid (OA) an unsaturated fatty acid obtained from Merck India and stearic acid (SA) which is saturated fatty acid obtained from Merck, Germany. Acetone (Merck, India) was used as solvent for dissolving and facilitating physical adsorption of carboxylic acids on alumina particle surface. A photocurable monomer 1, 6 Hexanedial diacrylate (HDDA, Sigma Aldrich, USA) which is a bifunctional, low viscous monomer (0.009Pas at 25°C) with -CH_2- terminated chain ends (hydrophobic backbone structure) was used. 1 –Hydroxy cyclohexyl phenyl ketone (HCPK) was used as photoinitiator. The molar extinction co-eff. of HCPK was found to be 35.67 M^{-1} cm^{-1}at 355nm measured by UV visible spectroscopy. The monomer was selected based on the criteria that are to be fulfilled by suspensions to qualify for stereolithography applications like low viscosity and refractive index matching with alumina etc. The molecular structures, properties of monomers, photoinitiator and dispersants are given table 1.

Table 1. Molecular structures and properties of monomers, photoinitiator and dispersants

Chemicals	Molecular structure	Refractive index	Density (g/cm^3)	Molecular Weight (g/mol)
1,6 Hexanediol diacrylate		1.456	1.01	226.27
Oleic acid		1.459	0.895	282.46
Stearic acid		1.429	0.847	284.48
1-Hydroxy cyclohexyl phenyl ketone		1.607	1.18	204.26

2.2 Experimental Method

Ceramic suspensions with solid loading of 0.35 volume fraction were prepared by dispersing surface modified alumina particles. Initially alumina powder was heated at 120°C in an oven under vacuum to remove moisture and

then dispersed in acetone along with different weight percentages of OA and SA separately. The suspension was pot milled for 24 hours using ceria stabilized zirconia balls of diameter 2-3mm in the ratio of 1:1 with respect to weight of powder. Then powder was dried at room temperature to remove acetone. The powder was heated at 130°C for chemical adsorption of OA and SA.

After chemical adsorption particles become hydrophobic in nature and are dispersed in HDDA incrementally till the solid volume fraction reaches to 0.35. Ceria stabilized zirconia balls in the ratio of 1:1 (on weight basis with respect to powder) were used to break down the agglomerates. 1-HCPK was added in suspension (1 wt. % with respect to weight of monomer). The suspensions were pot milled for about 12 hours to homogenize. Rheometer (Anton Paar Physica 301) was used to optimize dispersant quantity. The chemical bond formation between OA/SA and alumina surface was characterized using FTIR.

2.3 Experimental setup

Experimental setup shown fig 2 was used to fabricate ceramic components using constrained surface technique. The actual setup is shown along with schematic for better understanding. After fabrication of each layer the required amount of suspension was placed on previously fabricated layer and again scanned with UV light. This procedure was repeated until 5 layers were fabricated. After fabrication and cleaning the part with 2-propanol dimensions were measured with optical microscope (Olympus DP12) after cleaning with 2-propanol. Finally the part was sintered.

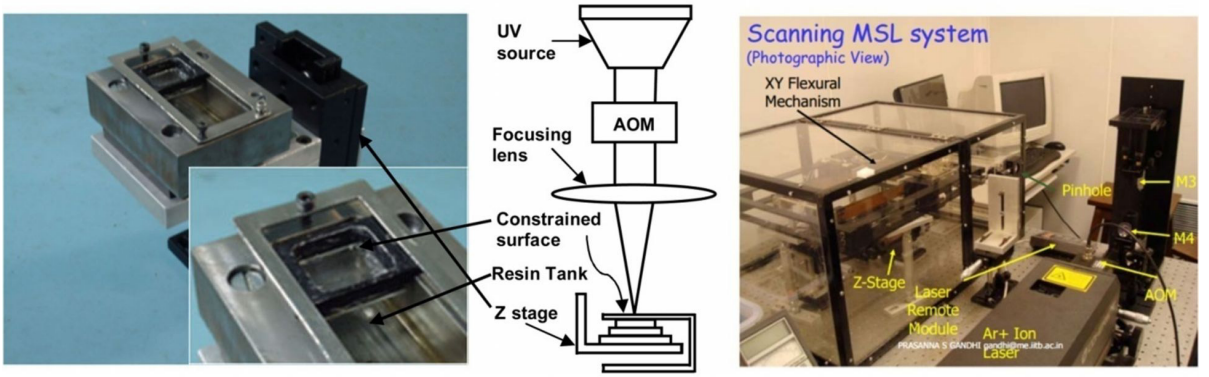


Figure 2 Actual setup of constrained surface and scanning based Microstereolithgraphy apparatus

3. Results and Discussion

3.1 Rheology of suspension

Optimum quantity of dispersant was determined from rheological experiments. The particle surface was modified with different weight percentages of OA and SA (from 0.5 to 2 wt. % with respect to weight of the powder) and rheological behavior was studied. Fig 3 shows rheological behavior of two ceramic suspensions, one was HDDA dispersed with alumina particles modified with OA and other HDDA dispersed with alumina particles modified by SA. Same loading of 0.35 volume fraction was maintained in each suspension. It was found that suspension of HDDA dispersed with 1.5 wt. % of OA is less viscous (2.23 Pas at 31.6 sec^{-1}) as compared to HDDA dispersed with 0.5 wt. % of SA (9.36 Pas at 31.6 sec^{-1}). Thus, HDDA suspension with dispersed alumina powder which was modified with oleic acid was chosen for the fabrication of ceramic parts. One of the criteria that has to be fulfilled by ceramic suspension for satisfactory layer recoating is 5Pas at 30 sec^{-1} shear rate [A. Licciulli et al. 2005]

3.2 FTIR characterization of surface modified alumina powder with oleic acid

The chemical bond formation between OA and ceramic particle surface was characterized by FTIR. The powders modified with various wt. % of OA were chosen and washed with acetone separately using centrifuge. Fig 4 shows FTIR spectra of modified powder and pure OA. For all powders modified by OA new peaks at 1468 and 1573 cm^{-1} appeared replacing COOH peak of OA at 1712cm^{-1}. These peaks indicate formation of chemical compound on the surface of alumina particles known as aluminium oleate. [Jen-Chieh et al. 2006; Leja John 1982] These powders after chemical modification became hydrophobic in nature and can be dispersed in HDDA easily.

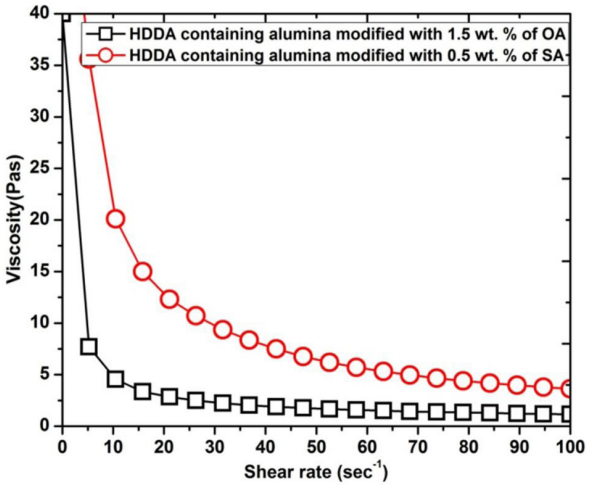


Figure 3. Rheology of suspension of HDDA dispersed with alumina modified with OA and SA

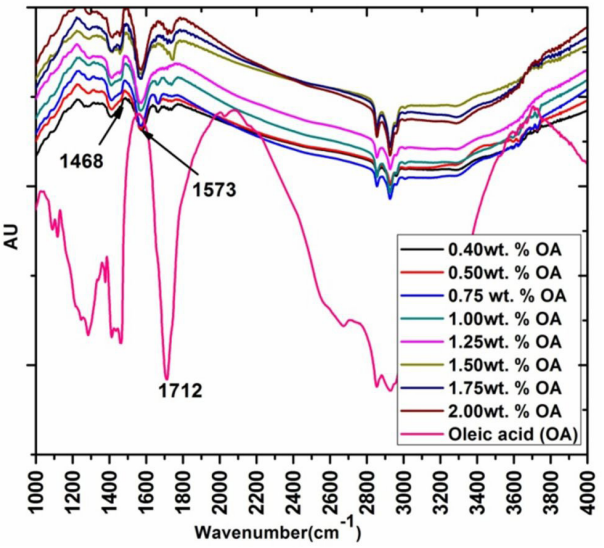


Figure 4. FTIR spectra of alumina powder modified with different weight percentages of OA

3.3 Fabrication of ceramic part

When UV curable ceramic suspension is exposed to UV light an inverted cone structure forms. The base of this cone is cure width and height of the cone is cure depth. Cure depth can be expressed as [Michelle L Griffith et al. 1996]

$$C_d = \left(\frac{d}{Q}\right)\left(\frac{1}{\Phi}\right) \ln\frac{E_{max}}{E_c} \tag{2}$$

E_c is the critical energy of exposure (the energy below which photopolymerization does not occur), E_{max} is the energy of exposure. 'Q' is the scattering efficiency term which depends upon refractive indices of the resin and ceramic particle, mean particle size and wavelength of UV light. Φ is the volume fraction of ceramic particles in the suspension. Cure width is function of spot size of UV light that can be expressed as

$$L_w = B\sqrt{\frac{C_d}{2D_p}} \tag{3}$$

Where B is the laser spot size, D_p is the depth of penetration. Cure depth of unfilled monomer is large due to absence of scattering effect. Cure depth should always be more than the layer thickness of part in order to fuse the layers together.

As a case study we have fabricated a frustum of cone with base diameter 1mm, height of 0.25mm and diameter at top 0.4mm.The z stage of MSL system was programmed to maintain a gap of 50 microns so that total build up

would comprise of 5 layers. Suspension of HDDA dispersed with alumina particles is placed on a glass slide of z stage and scanned with computer controlled laser. Laser spot size was 5 microns and laser power at source was 2mW, Scanning speed of laser was 1.2mm/sec. After fabrication it was noticed that out of five layers three were remained on the glass substrate and 2 were stuck on the constraining surface though there was no destruction of individual layers of the part. After fabrication of five layers the part was removed and cleaned with 2-propanol and dimensions are measured with optical microscope. The part was then subjected to debinding in a furnace at 600°C to burn out HDDA at temperature ramp of 2°C per minute and cooled down slowly to room temperature. Then the part was sintered at with temperature ramp of 5°C/min up to 1600°C and soaked at that temperature for about an hour. Fig 6 shows SEM images of as fabricated alumina part and sintered alumina part. The dimension of some of layers before sintering and after sintering are shown in table 2 The ceramic part shrinks in size owing to binder (HDDA) removal and densification during sintering process.

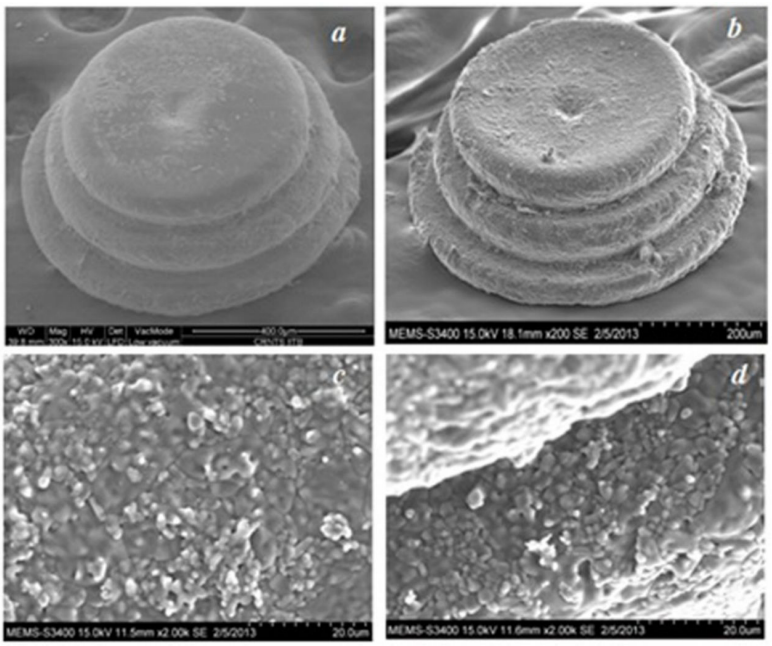


Figure 5. (a) SEM images of (a) as fabricated (b) sintered part (c) grain boundary structure (d) two different layers

Table 2. Dimensions of part before and after sintering and % shrinkage

Layers	Dimension in CAD (microns)	Dimensions before sintering (microns)	Dimension after sintering (microns)	% shrinkage
1st (bottom)	1000	830	530	36.14
2nd (Middle)	-	-	452	-
3rd (top)	-	600	380	36.67

4. Conclusion

Fabrication of ceramic part using constrained surface technique was demonstrated. This technique prove may prove to be better than doctor blade recoating technique in terms of uniform layer thickness and successive layer recoating in minimal time provided sticking of layers to the constraining surface is minimized. Though some layers of the part

stuck to constraining surface the layers constituting the part remain unaffected. Overall shrinkage of about 36% was observed after sintering the part. No micro cracks were observed during sintering due to shrinkage of part.

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